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(54) **Aluminium hydroxide and tyre tread rubber composition and pneumatic tyre employing the aluminium hydroxide**

(57) Aluminium hydroxide having specific characteristics, and a tyre tread rubber composition and a pneumatic tyre employing the aluminium hydroxide, which allow grip performance and abrasion resistance to increase and rolling resistance to decrease and are superior in processibility, are provided.

The aluminium hydroxide has a loosed bulk density of not more than 0.60g/cm<sup>3</sup>, a DOP oil absorption of at

least 70cm<sup>3</sup>/100g and less than 250cm<sup>3</sup>/100g, and a BET specific surface area of at least 30m<sup>2</sup>/g and not more than 350m<sup>2</sup>/g. 5-150 parts by weight of the aluminium hydroxide is blended with 100 parts by weight of a rubber component to obtain the tyre tread rubber composition. The rubber component preferably includes at least 60 parts by weight of styrene-butadiene rubber having a styrene content of 20-60% by weight.

## Description

## BACKGROUND OF THE INVENTION

[0001] The present invention relates to aluminium hydroxide, and a tyre tread rubber composition and a pneumatic tyre employing the aluminium hydroxide. More particularly, the present invention relates to aluminium hydroxide having specific characteristics; a tyre tread rubber composition having aluminium hydroxide blended therein, which allows grip performance on a wet road surface (wet grip performance) and abrasion resistance to increase and allows rolling resistance to decrease to improve fuel efficiency; and a pneumatic tyre employing the tyre tread rubber composition.

## DESCRIPTION OF THE BACKGROUND ART

[0002] In recent years, in response to the demands for fuel-efficient automobiles, fuel-efficient tyres with decreased rolling resistance have been developed. As a technique to decrease the rolling resistance, carbon black conventionally used as a reinforcing agent for tread rubber has been partially replaced with silica, in an effort to balance the antinomic properties of fuel efficiency and wet grip performance.

[0003] When compared to the conventional rubber composition with carbon black blended therein, however, the rubber composition with silica blended therein exhibits various problems in terms of processability. Specifically, it easily decomposes because of high viscosity of unvulcanisate, and is poor in dimensional stability after extrusion. Thus, a tread rubber composition satisfying both the processability and the performance has been desired.

[0004] Several techniques for improving the wet grip performance have also been proposed. One of such techniques is to increase the glass transition temperature ( $T_g$ ) of a rubber component, or, to increase the loss tangent ( $\tan\delta$  value) at  $0^\circ\text{C}$ .

Another technique is to blend carbon black of small particle size into a rubber composition with a high loading. If the glass transition temperature ( $T_g$ ) is increased, however, low temperature performance deteriorates and the rolling resistance increases. The rubber composition heavily-loaded with carbon black of small particle size also suffers a disadvantage that its rolling resistance increases.

## SUMMARY OF THE INVENTION

[0005] An object of the present invention is to provide a filler for a tyre, a tread rubber composition and a pneumatic tyre employing the same filler, that can solve the above-described problems by allowing wet grip performance and abrasion resistance to increase, rolling resistance to decrease for improvement of fuel efficiency, and achieving superior processability at the same time.

[0006] According to an aspect of the present invention, aluminium hydroxide is provided which has a loosed bulk density of not more than  $0.60\text{g/cm}^3$ , a DOP oil absorption of at least  $70\text{cm}^3/100\text{g}$  and less than  $250\text{cm}^3/100\text{g}$ , and a BET specific surface area of at least  $30\text{m}^2/\text{g}$  and not more than  $350\text{m}^2/\text{g}$ .

[0007] Particularly, a loosed bulk density of at least  $0.10\text{g/cm}^3$  and not more than  $0.35\text{g/cm}^3$  is preferable.

[0008] The aluminium hydroxide preferably has a crystal structure of boehmite type, having a crystal size of boehmite (002) plane of at least  $5\text{nm}$  and not more than  $20\text{nm}$ .

[0009] According to another aspect of the present invention, a tyre tread rubber composition is provided which is obtained by blending and kneading 5-150 parts by weight of the aluminium hydroxide as described above with 100 parts by weight of a rubber component.

[0010] The rubber component is preferably composed of at least 20 parts by weight of styrene-butadiene rubber having a glass transition temperature ( $T_g$ ) of not more than  $-27^\circ\text{C}$  and at least 20 parts by weight of diene type rubber including at least one kind of rubber selected from natural rubber, polyisoprene rubber and polybutadiene rubber. In the tyre tread rubber composition, 5-60 parts by weight of carbon black having a BET specific surface area of at least  $60\text{m}^2/\text{g}$  is preferably blended with respect of 100 parts by weight of the rubber component. Further, in the tyre tread rubber composition, 2-20% by weight of silane coupling agent is preferably blended with respect of the weight of the aluminium hydroxide.

[0011] Alternatively, the tyre tread rubber composition may employ a rubber component that includes at least 60 parts by weight of styrene-butadiene rubber having a styrene content of 20-60% by weight. 10-100 parts by weight of carbon black having a BET specific surface area of at least  $60\text{m}^2/\text{g}$  may be added with respect of 100 parts by weight of this rubber component, and/or 2-20% by weight of silane coupling agent may be blended with respect to the weight of the aluminium hydroxide.

[0012] According to a further aspect of the present invention, a pneumatic tyre is provided which employs the tyre tread rubber composition as described above.

[0013] The foregoing and other objects, features, aspects and advantages of the present invention will become

apparent from the following detailed description of the present invention.

## DESCRIPTION OF THE PREFERRED EMBODIMENTS

**[0014]** The aluminium hydroxide according to the present invention has a loosed bulk density, as measured conforming to JIS H1902, of not more than  $0.60\text{g/cm}^3$ , and preferably at least  $0.10\text{g/cm}^3$  and not more than  $0.35\text{g/cm}^3$ . If it is greater than  $0.60\text{g/cm}^3$ , abrasion resistance of the rubber composition considerably deteriorates. If it is low, torque when kneading the aluminium hydroxide and the rubber increases, thereby degrading the workability.

**[0015]** Further, the aluminium hydroxide described above has a DOP oil absorption, as measure conforming to JIS K6221, of at least  $70\text{cm}^3/100\text{g}$  and less than  $250\text{cm}^3/100\text{g}$ , and preferably at least  $90\text{cm}^3/100\text{g}$  and not more than  $150\text{cm}^3/100\text{g}$ . If it is out of such a range, the rubber composition suffers degradation of its abrasion resistance.

**[0016]** Still further, for the purposes of achieving a rubber composition having an effect to decrease the rolling resistance and exhibiting sufficient grip performance, the aluminium hydroxide has a BET specific surface area, as measured by nitrogen adsorption, of at least  $30\text{m}^2/\text{g}$  and not more than  $350\text{m}^2/\text{g}$ , preferably at least  $30\text{m}^2/\text{g}$  and not more than  $200\text{m}^2/\text{g}$ . If it exceeds  $350\text{m}^2/\text{g}$ , torque when kneading the aluminium hydroxide and the rubber may increase, thereby degrading workability.

**[0017]** Moreover, for the purposes of further improving the grip performance, the abrasion resistance and the effect to decrease the rolling resistance of the rubber composition, the aluminium hydroxide of the present invention preferably has a crystal structure of boehmite type. More preferably, the crystal size of boehmite (020) plane is at least 5nm and not more than 20nm.

**[0018]** The crystal size was calculated as follows. Peaks of the boehmite (020) planes were measured from the profile obtained using an X-ray diffractometer. For these peaks of the crystal planes, fitting was conducted, based on the Gaussian distribution, using software for "multi-peak separation" of RINT 2100. Using the half-value width of the calculated result and the peak angle obtained by the barycentric method, the crystal size was calculated by the Scherrer's formula. The measurement conditions for the X-ray diffraction were as follows:

Measurement device: Rint-2100V from Rigaku International Corporation.

Measurement conditions: Cu target; Voltage x Current = 40 kV x 40 mS; Slit:  $\text{DS}1^\circ$  -  $\text{SS}1^\circ$  - RS 0.3mm; Scan mode: continuous; Scan speed =  $2^\circ/\text{min}$ ; Scan step =  $0.010^\circ/\text{step}$ ; Scan axis  $2\theta/\theta$ ; Scan range:  $2-70^\circ$ ; and Rotation speed: 0 rpm.

**[0019]** A blended amount of the aluminium hydroxide described above is 5-150 parts by weight, preferably 5-80 parts by weight, and particularly 5-60 parts by weight with respect to 100 parts by weight of the rubber component described above. If it is less than 5 parts by weight, the decrease of the rolling resistance by virtue of such addition is not adequate, and the grip performance against a wet road surface is improved only to a small extent. If the blended amount exceeds 150 parts by weight, viscosity of the rubber composition becomes too high, which deteriorates the processibility as well as the abrasion resistance.

**[0020]** One way of producing the aluminium hydroxide of the present invention is as follows. Aluminium alkoxide is hydrolysed to obtain a slurry of aluminium hydroxide, which is passed through a continuous wet grinder or the like to obtain a suspension. The obtained suspension is alkalised, then subjected to heat treatment at about  $100^\circ\text{C}$  to  $140^\circ\text{C}$  for about 10 hours to 100 hours, and then dried using a flash dryer or the like. In this method of producing the aluminium hydroxide, it is preferable that the suspension having undergone the heat treatment is subjected to solid-liquid separation to extract the solid content (aluminium hydroxide), and then the solid content is washed to remove impurities.

**[0021]** In the present invention, various kinds of rubber that are generally used for a tyre tread rubber, e.g. natural rubber, polyisoprene rubber and polybutadiene rubber, may be used as a rubber component.

**[0022]** The rubber component employed in the present invention preferably includes at least 20 parts by weight of styrene-butadiene rubber having a glass transition temperature ( $T_g$ ) of not more than  $-27^\circ\text{C}$ . conventionally, in order to balance the antinomic properties of improved wet grip performance and decreased rolling resistance, styrene-butadiene rubber with a relatively high glass transition temperature ( $T_g$ ) has been employed. In this case, however, there is a limit for the improvement of the rolling resistance, and the abrasion resistance tends to be degraded. Thus, according to the present invention, the glass transition temperature ( $T_g$ ) of styrene-butadiene rubber is made not to exceed  $-27^\circ\text{C}$  so as to improve the rolling resistance. For the purposes of maintaining good wet grip performance, the styrene-butadiene rubber is preferably made to have a glass transition temperature in a range between  $-0^\circ\text{C}$  and  $-50^\circ\text{C}$ , and more preferably, at least 50 parts by weight thereof is blended in the rubber component.

**[0023]** When employing such a rubber component, the aluminium hydroxide is preferably added at 5-60 parts by weight with respect to 100 parts by weight of the rubber component.

**[0024]** In this case, at least 20 parts by weight of at least one kind of rubber selected from natural rubber (NR), polyisoprene rubber (IR), low cis-polybutadiene rubber (low cis-BR) and high cis-polybutadiene rubber (high cis-BR)

is also includes as another rubber component. Preferably, these rubber components each have a glass transition temperature (T<sub>g</sub>) of not more than -27°C, and work together with the above-described styrene-butadiene rubber to improve the wet grip performance, rolling resistance and abrasion resistance, totally in a well balanced manner.

**[0025]** As another embodiment of the present invention, the rubber component being used for the tyre tread rubber composition preferably includes styrene-butadiene rubber having a styrene content of 20-60% by weight. If the styrene content is less than 20% by weight, the grip performance in the low and high temperature regions is not improved. If it exceeds 60% by weight, block rigidity increases, so that the "bite" if the rubber on contact with the road surface becomes poor, making it impossible to achieve a desired gripping force. In particular, the styrene content of 30-45% by weight is preferable. Such styrene-butadiene rubber is synthesised by emulsion polymerisation, solution polymerisation or the like.

**[0026]** When employing such a rubber component, the aluminium hydroxide is preferably blended 5-80 parts by weight with respect to 100 parts by weight of the rubber component.

**[0027]** Here, other rubber components that may be used for the tyre tread rubber composition include: natural rubber (NR), high cis 1,4-polybutadiene rubber, low cis 1,4-polybutadiene rubber, styrene-butadiene rubber (SBR) other than as described above, polyisoprene rubber (IR), butyl rubber (IIR), halogenated butyl rubber, acrylonitrile-butadiene rubber (NBR), acrylonitrile-styrene-butadiene rubber, chloroprene rubber, ethylene-propylene copolymer rubber, styrene-isoprene copolymer rubber, styrene-isoprene-butadiene copolymer rubber, isoprene-butadiene copolymer rubber, chlorosulfonic polyethylene, acrylic rubber, epichlorohydrin rubber, silicone rubber and urethane rubber. Any of them may be used alone, or at least two kinds thereof may be blended together in any arbitrary proportions. In particular, for the purposes of improving processibility and abrasion resistance, NR, BR, SBR, IR, styrene-isoprene-butadiene copolymer rubber and the like are preferable.

**[0028]** Preferably, at least 60 parts by weight of the styrene-butadiene rubber having a styrene content within the above described range is blended into the rubber component for use in the present invention.

**[0029]** If the blended amount of the styrene-butadiene rubber is less than 60 parts by weight, the grip performance in the low and high temperature regions cannot be improved.

**[0030]** Further, the carbon black being blended into the tread rubber composition of the present invention preferably has a BET specific surface area, as measured by nitrogen adsorption, of at least 60m<sup>2</sup>/g, preferably 70-220m<sup>2</sup>/g, and more preferably 70-200m<sup>2</sup>/g. The BET specific surface area of less than 60m<sup>2</sup>/g is not preferable, since an adequate level of abrasion resistance cannot be expected. Here, the BET specific surface area was measured conforming to the ASTM D 4820-99 method.

**[0031]** If the carbon black is being blended into a rubber component including at least 60 parts by weight of styrene-butadiene rubber having a styrene content of 20-60% by weight, the blended amount of the carbon black is 10-100 parts by weight, preferably 30-100 parts by weight, and more preferably 40-100 parts by weight, with respect to 100 parts by weight of the rubber component. If the weight of the carbon black is less than 10 parts by weight, abrasion resistance is deteriorated. If it exceeds 100 parts by weight, viscosity of the rubber increases, thereby degrading the processibility.

**[0032]** In the case where the carbon black is being blended into a rubber component including at least 20 parts by weight of styrene-butadiene rubber having a glass transition temperature (T<sub>g</sub>) of not more than -27°C, the blended amount of the carbon black is 5-60 parts by weight, preferably 10-60 parts by weight, and more preferably 20-60 parts by weight, with respect of 100 parts by weight of the rubber component. If it is less than 5 parts by weight, abrasion resistance becomes, poor. If it exceeds 60 parts by weight, viscosity of the rubber increases, thereby deteriorating the processibility.

**[0033]** Still further, for the purposes of further reinforcing the aluminium hydroxide, 2-20% by weight of silane coupling agent may be added with respect to the blended amount of aluminium hydroxide. The silane coupling agents that may be used here include: bis(3-triethoxysilylpropyl)tetrasulfide, bis(2-triethoxysilylethyl)tetrasulfide bis(3-trimethoxysilylpropyl) tetrasulfide, bis(2-trimethoxysilylethyl)tetrasulfide, 3-mercaptopropyltrimethoxysilane, 3-mercaptopropyltriethoxysilane, 2-mercaptopropyltrimethoxysilane, 2-mercaptopropyltriethoxysilane, 3-nitropropyltrimethoxysilane, 3-nitropropyltriethoxysilane, 3-chloropropyltrimethoxysilane, 3-chloropropyltriethoxysilane, 2-chloroethyltrimethoxysilane, and 2-chloroethyltriethoxysilane. Among them, bis(3-triethoxysilylpropyl)tetrasulfide is preferable for balancing the cost and the effect expected by adding the coupling agent.

**[0034]** The rubber composition of the present invention may be used together with other fillers, such as silica, clay or the like. It may also be blended, if necessary, with various kinds of additives including process oil, antioxidant, stearic acid, zinc oxide and wax, and of course with vulcanising agents such as sulfur, vulcanisation accelerator or the like.

**EXAMPLES**Examples A, B and Comparative Examples C, D and E

- 5 [0035] The aluminium hydroxide employed in each of these examples and comparative examples was produced as follows. Characteristic values thereof are shown in Table 1.

Example A (aluminium hydroxide A)

- 10 [0036] 376g of aluminium hydroxide (loosed bulk density: 0.77g/cm<sup>3</sup>, DOP oil absorption: 70cm<sup>3</sup>/100g) obtained by hydrolysing aluminium alkoxide was mixed with 5dm<sup>3</sup> of water, and suspension having a solid content of 7% by weight was prepared. The suspension was passed through a continuous bead mill to let the aluminium hydroxide uniformly disperse in the suspension. The suspension after such dispersion was put into a stainless beaker, and adjusted to have a pH of 10 using 1N NaOH. With a refluxing device attached to the stainless beaker, the suspension within the
- 15 stainless beaker was heated, left at 100°C for 60 hours, and gradually cooled. The suspension was then separated to solid and liquid employing a centrifugal separator. After removing the supernatant liquid, the solid content was dispersed in 5dm<sup>3</sup> of water added. A centrifugal separator was again used for solid-liquid separation thereof. The solid content thus obtained was dispersed in 5dm<sup>3</sup> of newly added water to obtain slurry of aluminium hydroxide, which was passed through a continuous bead mill, and then dried with a flash dryer (trade mark: Flash Jet Dryer, manufactured by Seishin Enterprise Co., Ltd.). aluminium hydroxide A was thus obtained.
- 20 [0037] Physical properties of the aluminium hydroxide A obtained are shown in Table 1.

Example B (aluminium hydroxide B)

- 25 [0038] 376g of aluminium hydroxide (loosed bulk density: 0.77g/dm<sup>3</sup>, DOP oil absorption: 70cm<sup>3</sup>/100g) obtained by hydrolysing aluminium alkoxide was mixed with 5dm<sup>3</sup> of water, and suspension having a solid content of 7% by weight was prepared. 1N NaOH was used to set a pH of this suspension to 10. The suspension was then put into an autoclave and held at 120°C for 24 hours. The suspension was gradually cooled, and then subjected to solid-liquid separation employing a centrifugal separator. After removing the supernatant liquid, the solid content was dispersed in 5dm<sup>3</sup> of
- 30 water added. Solid-liquid separation was conducted again using a centrifugal separator. The solid content obtained was dispersed in 5dm<sup>3</sup> of newly added water to obtain slurry of aluminium hydroxide, which was passed through a continuous, bead mill, and then dried using a flash dryer (trade name: Flash Jet Dryer, manufactured by Seishin Enterprise Co., Ltd.). Aluminium hydroxide B was thus obtained.
- [0039] Physical properties of the obtained aluminium hydroxide B are shown in Table 1.

Comparative Example C (aluminium hydroxide C)

- [0040] 533cm<sup>3</sup> of sodium alminate solution (sodium concentration: 125g/dm<sup>3</sup> in terms of Na<sub>2</sub>O, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar ratio: 1.55) as a basic solution and 880cm<sup>3</sup> of aqueous aluminium sulfate solution (aluminium concentration: 5.3% by
- 40 weight in terms of Al<sub>2</sub>O<sub>3</sub>) as an acid solution were injected into a 2dm<sup>3</sup> stainless bath provided with a baffle for about three minutes for neutralisation. During the injection, the solution were being cooled with ice and stirred using a homo-mixer (trade name: T.K. Homo-Jetter M type, manufactured by Tokushu Kika Kogyo Co., Ltd.) under the condition of shear rate of 11000sec<sup>-1</sup>. (The shear rate was derived from the peripheral velocity of the turbine of the homo-mixer, x m/sec, and the clearance between the turbine and the status y mm, using an expression of  $x/y \times 10^3 \text{ sec}^{-1}$ ). Thereafter, the stirring was continued for 15 minutes to obtain slurry of aluminium hydroxide. The maximum reachable temperature at the time of neutralisation was 15°C.

[0041] A centrifugal separator was used for solid-liquid separation of the obtained slurry of aluminium hydroxide to extract the solid content. The solid content obtained was dispersed in 6dm<sup>3</sup> of water added, to obtain slurry of aluminium hydroxide.

- 50 [0042] Thereafter, solid-liquid separation using a centrifugal separator was repeated seven times to wash the aluminium hydroxide. Water was added to the solid content extracted after such washing to obtain slurry of aluminium hydroxide, which was then dried using a spray dryer (from Niro A/S, trade name: Mobile Minor Type, drying temperature: 250°C at dryer inlet and 100°C at dryer outlet, atomising pressure: 0.12 MPa). Aluminium hydroxide C was thus obtained, of which physical properties are shown in Table 1.

Comparative Example D (aluminium hydroxide D)

- [0043] 800cm<sup>3</sup> of sodium alminate solution (sodium concentration: 125g/dm<sup>3</sup> in terms of Na<sub>2</sub>O, Na<sub>2</sub>O/Al<sub>2</sub>O<sub>3</sub> molar

ratio 1.55) as a basic solution and 898cm<sup>3</sup> of aqueous aluminium sulfate solution (aluminium concentration: 3.2% by weight in terms of Al<sub>2</sub>O<sub>3</sub>) as an acid solution were injected into a 2dm<sup>3</sup> stainless bath provided with a baffle for three minutes for neutralisation. During the injection, the solutions were being cooled with ice and stirred using a homo-mixer (trade name: T.K. Homo-Jetter M type, manufactured by Tokushu Kika Kogyo Co., Ltd.) under the condition of shear rate of 11000 sec<sup>-1</sup>. Thereafter, the stirring was continued for 15 minutes to obtain slurry of aluminium hydroxide. The maximum reachable temperature at the time of neutralisation was 15°C. A centrifugal separator was used for solid liquid separation of the obtained slurry of aluminium hydroxide to extract the solid content. The solid content obtained was dispersed in 6dm<sup>3</sup> of water added, so that slurry of aluminium hydroxide was obtained. Thereafter, solid liquid separation employing a centrifugal separator was repeated seven times to wash the aluminium hydroxide. Water was added to the solid content extracted after such washing to obtain slurry of aluminium hydroxide, which was then dried using a spray drying (from Niro A/S, trade name: Mobile Minor Type, drying temperature: 250°C at dryer inlet and 100°C at dryer outlet, atomising pressure: 0.12 MPa). Aluminium hydroxide D was thus obtained. Physical properties of the obtained aluminium hydroxide D are shown in Table 1.

#### Comparative Example E (aluminium hydroxide E)

**[0044]** Commercially available aluminium hydroxide (manufactured by Showa Denko K.K., trade name: Higilite H-43) was used without alteration.

**[0045]** As shown in Table 1, aluminium hydroxide C of Comparative example C and aluminium hydroxide of Comparative example D each have a greater loosed bulk density and a smaller crystal size of boehmite (020) plane as compared with those of Examples A and B. Aluminium hydroxide E of Comparative example E has a BET specific surface area and a DOP oil absorption both smaller than those of Examples A and B, and its crystal structure is gibbsite, which is different from boehmite of Examples A and B.

TABLE 1

Kinds of aluminium hydroxide	Physical properties				
	Loosed bulk density g/cm <sup>3</sup>	DOP oil absorption: cm <sup>3</sup> /100g	BET specific surface area: m <sup>2</sup> /g	Crystal structure	Crystal size of boehmite (020) plane: nm
Example A	0.21	121	153	boehmite	12.9
Example B	0.33	80	208	boehmite	7.3
Comparative example C	0.94	54	250	boehmite	2.4
Comparative example D	0.61	84	110	boehmite bayerite	3.0
Comparative example E	0.20	55	8	Gibbsite	-

Examples 1-11 and Comparative Examples 1-12

[0046] Tyre tread rubber compositions and tyres were produced as follows.

[0047] Ingredients as shown in Tables 2 and 3 were blended as specified therein, and kneaded using a Banbury

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mixer to prepare respective rubber compositions. Processibility (Mooney viscosity) thereof was evaluated. Thereafter, an extruder was used to extrude the respective rubber compositions each into a tread shape, which was vulcanised in a mould to manufacture by trial a tyre of a size of 185/65R14. For each tyre obtained, abrasion resistance, rolling resistance and wet grip performance (ABS braking) were evaluated. The evaluation results are shown in Tables 2 and 3.

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TABLE 2

	(Parts by weight)	Examples					Comparative examples					
		1	2	3	4	5	1	2	3	4	5	6
Ingredients	SBR N 9520 (pure polymer)	X1)	70	70	70	50	70	70	70	70	70	70
	BR 150B	X2)	30	30	30	50	30	30	30	30	30	30
	Carbon black N220	X3)	65	65	40	40	65	65	65	65	65	65
	Aluminium hydroxide A		40		65	65	40					
	Aluminium hydroxide B			40								
	Aluminium hydroxide C									40		
	Aluminium hydroxide D										40	
	Aluminium hydroxide E											40
	Silica VN3	X4)					40					
	TESPT	X5)				5.2	3.2					
	Aromatic oil (incl. oil extended polymer)	X6)	40	40	35	40	40	35	50	45	45	45
Evaluation	Antioxidant	X7)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	WAX	X8)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Stearic acid	X9)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Zinc oxide	X10)	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0	3.0
	Sulfur	X11)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
	Vulcanisation accelerator	X12)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
	Mooney viscosity		105	106	105	107	105	100	100	108	106	104
	Abrasion resistance		100	98	98	103	103	95	100	74	65	81
	Rolling resistance		108	110	113	118	113	125	100	108	110	111
	Wet grip performance (ABS braking)		111	109	112	115	87	82	100	105	106	106

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[0048] Details of the ingredients shown in Table 2 are as follows:

X1) SBR: styrene-butadiene rubber N9520 (from Nippon Zeon Corporation), styrene content: 35% by weight, 37.5 PHR oil extended rubber, glass transition temperature (T<sub>g</sub>): -38°C.

X2) BR: polybutadiene rubber BR150B (from Ube Industries Ltd.).

X3) carbon black: Diablack I (N220, from Mitsubishi Chemical Corporation), BET specific surface area by nitrogen adsorption: 115m<sup>2</sup>/g.

X4) silica: VN3 (from Degussa).

X5) silane coupling agent TESPT: Si-69 (from Degussa).

X6 aromatic oil: Diana Process PS32 (from Idemitsu Kosan Co., Ltd.).

X7 antioxidant: Ozonon 6C from (Seiko Chemical Co., Ltd.).

X8 WAX: Sannoc Wax (from Ouchishinko Chemical Industrial Co., Ltd.).

X9 stearic acid: Kiro (from NOF Corp.).

X10 ZINC OXIDE: Zinc Oxide #2 (from Mitsui Mining & Smelting Co., Ltd.).

X11 sulfur: Sulfur (from Karuizawa Seirenscho Co. Ltd.).

X12 vulcanisation accelerator: Noceler CZ (from Ouchishinko Chemical Industrial Co., Ltd.).

TABLE 3

	(Parts by weight)	Examples						Comparative examples							
		6	7	8	9	10	11	7	8	9	10	11	12		
Ingredients	SBR 1502	X1)	70	70	70	70	100	-	70	70	70	70	70	70	
	NR	X2)	30	30	30	30		30	30	30	30	30	30	30	
	SBR N9550	X3)						70							
	Carbon black N339	X4)	40	40	40	40	40	40	40	60	40	40	40	40	
	Aluminium hydroxide A		20		30	20	20	20							
	Aluminium hydroxide B			20											
	Aluminium hydroxide C													20	
	Aluminium hydroxide D											20			
	Aluminium hydroxide E														
	Silica VN3	X5)								20			20		
	TESPT	X6)							2	2					
Evaluation	Aromatic oil	X7)	15	15	10	15	15	15	20	10	20	15	15	15	
	Antioxidant	X8)	20	20	20	20	20	20	20	20	20	20	20	20	
	WAX	X9)	20	20	20	20	20	20	20	20	20	20	20	20	
	Stearic acid	X10)	20	20	20	20	20	20	20	20	20	20	20	20	
	Zinc oxide	X11)	30	30	30	30	30	30	30	30	30	30	30	30	
	Sulfur	X12)	20	20	20	20	20	20	20	20	20	20	20	20	
	Vulcanisation accelerator		10	10	10	10	10	10	10	10	10	10	10	10	
	Mooney viscosity		95	97	95	98	95	102	120	95	100	96	94	98	
	Abrasion resistance		100	98	98	103	102	100	94	80	100	69	85	78	
	Rolling resistance		110	112	115	118	88	80	109	121	100	112	111	110	
	Wet grip performance (ABS braking)		111	110	112	114	110	120	105	82	100	106	106	105	

Details of the ingredients shown in Table 3 are as follows:

X1) SBR: styrene-butadiene rubber SBR 1502 (from Sumitomo Chemical Co., Ltd.), glass transition temperature (T<sub>g</sub>): -48°C, styrene content: 23.5% by weight.

X2) NR: natural rubber RSS#1.

X3) SBR: styrene-butadiene rubber N9550 (from Nippon Zeon Corporation), glass transition temperature (T<sub>g</sub>): -26°C, styrene content: 45% by weight.

X4) carbon black; Sho Black N339 (from Showa Cabot K.K.), BET specific surface area by nitrogen adsorption: 90m<sup>2</sup>/g.

X5) silica: VN3 (from Degussa).

X6) silane coupling agent TESPT: Si-69 from Degussa).

X7) aromatic oil: Diana Process PS32 (from Idenitsu Kosan Co., Ltd.).

X8) antioxidant: Ozonon 6C (from Seiko Chemical Co., Ltd.).

X9) WAX: Sannoc Wax (from Ouchishinko Chemical Industrial Co., Ltd.).

X10) stearic acid: Kiri (from NOF Corp.).

X11) zinc oxide: Zinc Oxide #2 (from Mitsui Mining & Smelting Co., Ltd.).

X12) sulfur: Sulfur (from Karuizawa Seirenscho Co., Ltd.).

X13) vulcanisation accelerator: Nocceler CZ (from Ouchishinko Chemical Industrial Co., Ltd.).

**[0049]** Evaluation methods employed for Examples 1-11 and Comparative examples 1-12 are as follows:

#### 1. Mooney Viscosity ML (1+4)

**[0050]** The Mooney viscosity was measured using MV-202 (from Shimadzu Corporation, conforming to JIS K6300. The measurements were represented as indices, with those for Comparative example 3 in Table 2 and Comparative example 9 in Table 3 being respectively set to 100. The measurement was performed at 130°C. The greater the index, the poorer the factors of processibility, such as extrusion, become.

#### 2. Abrasion Resistance

**[0051]** An abrasion resistance test was conducted using a Lambourn abrasion tester FR-702 (from Iwamoto Seisakusho Co., Ltd.), conforming to JIS K6264. The measurement was performed at 23°C for five minutes, with a slip ratio of 30% and applying load of 40N, to measure the volume of abrasion loss. The measurements were represented as indices, with those for Comparative example 3 in Table 2 and Comparative example 9 in Table 3 being respectively set to 100. The greater the index, the better the abrasion resistance becomes.

#### 3. Rolling Resistance

**[0052]** The rolling resistance was measured using a drum type rolling resistance measuring device having a diameter of 1707.6mm (from Kobe Steel Ltd.). The measurements were represented as indices, with those for Comparative example 3 in Table 2 and Comparative example 9 in Table 3 being respectively set to 100. The greater the index, the lower the rolling resistance becomes. The measurement conditions were as follows: internal pressure: 200 Kpa, load: 3.4 KN, rim: 5.5 JJ x 14, speed: 80km/h.

#### 4. Wet Grip Performance (ABS Braking)

**[0053]** Tyres were attached to a passenger car of 1800cc class provided with ABS (Antilock Braking System), and deceleration was calculated from a stopping distance from 100km/h on an asphalt-paved road surface. The calculated results were represented as indices, with those for Comparative example 3 in Table 2 and Comparative example 9 in Table 3 being respectively set to 100. The greater the index, the more the brakeage, and accordingly the grip performance improves. The road surface used for the ABS braking test was the asphalt-paved road surface with a skid number of about 50 (wet road surface condition).

**[0054]** Referring to Table 2, Comparative example 1 using silica exhibits high Mooney viscosity, which means that the processibility is poor. Comparative example 2 having no aluminium hydroxide blended therein is inferior in ABS braking. Comparative example 4 using aluminium hydroxide C whose crystal size of boehmite (020) plane is small and whose loosed bulk density is great, Comparative example 5 using aluminium hydroxide D, and Comparative example 6 using aluminium hydroxide E whose BET specific surface area is small and whose crystal structure is of gibbsite type, all exhibit considerably poor abrasion resistance.

[0055] In contrast to these comparative examples, Examples 1-4 are significantly improved in rolling resistance and wet grip performance (ABS braking), without their processibility or abrasion resistance being sacrificed. Example 5 containing less than 60 parts by weight of styrene-butadiene rubber having a styrene content of 20-60% by weight is slightly inferior in ABS braking.

[0056] Referring to Table 3, Comparative example 7 using silica exhibits high Mooney viscosity, which means it is poor in processibility. Comparative example 8 having no aluminium hydroxide blended therein is inferior in ABS braking. Comparative example 12 using aluminium hydroxide C whose crystal size of boehmite (020) plane is small and whose loosed bulk density is great, Comparative example 10 using aluminium hydroxide D, and Comparative example 11 using aluminium hydroxide E whose BET specific surface area is small and whose crystal structure is of gibbsite type, all exhibit considerably degraded abrasion resistance.

[0057] In contrast to these comparative examples, Examples 6-9 exhibit greatly improved rolling resistance and wet grip performance (ABS braking), without their processibility or abrasion resistance being deteriorated. Example 10 not including natural rubber (NR), polyisoprene rubber (IR) or polybutadiene rubber (BR), and Example 11 employing styrene-butadiene (SBR) whose glass transition temperature (T<sub>g</sub>) is higher than -27°C, are both slightly inferior in rolling resistance.

[0058] As explained above, aluminium hydroxide of the present invention possess specific characteristics. A tyre tread rubber composition having such aluminium hydroxide blended therein allows wet grip performance and abrasion resistance to increase, rolling resistance to decrease to improve fuel efficiency, and enjoys improved processibility. A pneumatic tyre employing such a tread rubber composition is also superior in these characteristics.

[0059] Although the present invention has been described and illustrated in detail, it is clearly understood that the same is by way of illustration and example only and is not to be taken by way of limitation, the spirit and scope of the present invention being limited only by the terms of the appended claims.

## Claims

1. Aluminium hydroxide characterised by a loosed bulk density of not more than 0.60g/cm<sup>3</sup>, a DOP oil absorption of at least 70cm<sup>3</sup>/100g and less than 250cm<sup>3</sup>/100g, and a BET specific surfaced area of at least 30m<sup>2</sup>/g and not more than 350m<sup>2</sup>/g.
2. The aluminium hydroxide according to claim 1, characterised in that the loosed bulk density is at least 0.10g/cm<sup>3</sup> and not more than 0.35g/cm<sup>3</sup>.
3. The aluminium hydroxide according to claim 1 or 2, characterised by a crystal structure of boehmite type.
4. The aluminium hydroxide according to claim 3, characterised by a crystal size of boehmite (020) plane of at least 5nm and not more than 20nm.
5. A tyre tread rubber composition characterised by 5-150 parts by weight of the aluminium hydroxide according to claim 1 blended with 100 parts by weight of a rubber component.
6. A tyre tread rubber composition according to claim 5, characterised in that the rubber component is composed of at least 20 parts, by weight of styrene-butadiene rubber having a glass transition temperature (T<sub>g</sub>) of not more than -27°C and at least 20 parts by weight of diene type rubber including at least one kind of rubber selected from natural rubber, polyisoprene rubber and polybutadiene rubber.
7. A tyre tread rubber composition according to claim 6, characterised by 5-60 parts by weight of carbon black having a BET specific surface area of at least 60m<sup>2</sup>/g blended with respect to 100 parts by weight of the rubber component.
8. A tyre tread rubber composition according to claim 6 or 7, characterised by 2-20% by weight of silane coupling agent blended with respect to the weight of said aluminium hydroxide.
9. A tyre tread rubber composition according to claim 5, characterised in that the rubber component includes at least 60 parts by weight of styrene-butadiene rubber having a styrene content of 20-60% by weight.
10. A tyre tread rubber composition according to claim 9, characterised in that 10-100 parts by weight of carbon black having a BET specific surface area of at least 60m<sup>2</sup>/g blended with respect to 100 parts by weight of the rubber component.

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11. A tyre tread rubber composition according to claim 10, characterised by 2-20% by weight of silane coupling agent blended with respect to the weight of said aluminium hydroxide.
12. A pneumatic tyre characterised by a tyre tread rubber composition according to any of claims 5 to 11.

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# EUROPEAN SEARCH REPORT

Application Number  
EP 00 31 1658

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CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date O : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			

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